An Improved Method of Moments as a More Reliable Alternative for Prediction of Average Molecular Weights of Irreversible Non-Linear Polymerizations and Reversible Polycondensations

Rolando C. S. Dias[1], Mário Rui P. F. N. Costa[2]

[1] LSRE, Instituto Politécnico de Bragança, Quinta de S. Apolónia, 5300 Bragança, Portugal

[2] LSRE, Faculdade de Engenharia da Universidade do Porto, Rua Roberto Frias s/n, 4200-465 Porto, Portugal

Summary

Mass balance equations of polymer species in ideal reactors yield first-order partial differential equations in terms of generating functions when dealing with homogeneous non-linear irreversible polymerizations, as also do simple linear reversible polycondensations. Their numerical solution using the method of characteristics is often plagued by problems of numerical sensitivity, which only recently could be reliably overcome [1]. Besides allowing prediction of chain length distributions (not here discussed) an efficient prediction of average molecular weights even in the presence of gel is possible. Free-radical polymerization with transfer to polymer and vinyl/divinyl metallocene catalyzed copolymerization are discussed. Inherent weaknesses of "numerical fractionation" are unveiled through comparison with these results.

Description of Linear Reversible Polycondensations and Closure Problems

It is enlightening to start by writing mass balance equations in a batch reactor (without volume change) of a simplified single monomer reversible polycondensation, such as Nylon 6 formation, taking into account the presence of monomer rings C_1 (see Table 1):

$$\frac{d[P_x]}{dt} = \delta_x^1\left(k_{h_1}[W][C_1] - k_{c_1}[P_1] + k_{ce}[P_1]\right) +$$
$$k_p[C_1]([P_{x-1}] - [P_x]) + k_{ce}([P_{x+1}] - [P_x]) +$$
$$k\left(\sum_{y=1}^{x-1}[P_y][P_{x-y}] - 2[P_x]\sum_{y=1}^{\infty}[P_y]\right) +$$
$$k_h[W]\left[2\sum_{y=1}^{\infty}[P_y] - 2\sum_{y=1}^{x-1}[P_y] - (x+1)[P_x]\right] + \qquad (1)$$
$$k_e\left[\left(\sum_{y=1}^{\infty}[P_y]\right)^2 - \sum_{y=1}^{x-1}[P_y]\sum_{z=1}^{x-y}[P_z] -\right.$$
$$\left.\left(x\sum_{y=1}^{\infty}[P_y] + \sum_{y=1}^{\infty}(y-1)[P_y]\right)[P_x]\right]$$
$$\frac{d[C_1]}{dt} = -k_{h_1}[W][C_1] + k_{c_1}[P_1] + k_{ce}\left(\sum_{y=1}^{\infty}[P_y] - [P_1]\right) - k_p[C_1]\sum_{y=1}^{\infty}[P_y]$$

Mass balance equations of the first N polymer species P_1 ... P_N do not form a closed set of equations, because $[P_N]$ depends on $[P_{N+1}]$ and so on. A first order partial differential equation (PDE) in terms of moment generating function $G = \sum_{x=1}^{\infty} s^x[P_x]$ results:

$$\frac{\partial G}{\partial t} = \frac{\partial \sum_{x=1}^{\infty} s^x[P_x]}{\partial t} = s\left(k_{h_1}[W][C_1] - k_{c_1}[P_1]\right) + k_p[C_1](s-1)G +$$
$$k_{ce}(1-s)\left(G/s - [P_1]\right) + kG(G - 2\lambda_0)$$
$$+k_h[W]\left(2\frac{\lambda_0 s - G}{1-s} - \frac{\partial G}{\partial \log s} + G\right) + \qquad (2)$$
$$k_e\left[\frac{\lambda_0 s - G}{1-s}(\lambda_0 + G) - \lambda_0\frac{\partial G}{\partial \log s} + (2\lambda_0 - \lambda_1)G\right]$$

In the classical "method of moments", differentiation of the above equation over $s = 1$ is used to obtain equations allowing to predict the first moments of CLD (chain length distribution) $[P_x]$. But here this operation will not yield a closed set of equations: the equation for N-th order moment $\lambda_N = \sum_{x=1}^{\infty} x^N[P_x]$ involves also moment λ_{N+1} and so on.

This is often circumvented by assuming the CLD can be expanded as a series of orthogonal functions (such as modified Laguerre functions), and so all higher order moments would be related to the N lowest order moments on truncation to the first N terms of the series. The most popular closure assumption of this kind is due to Hulburt and Katz [2] and in its simplest version will yield a relation between the third and second moments of CLD, or a hopefully more exact higher order relationship.

The more exact approach (an "improved" method of moments), which the authors recommend, consists in numerically solving the PDE, which can be done using the method of characteristics. Space limitations prevent us from presenting an algorithm modified from a previous work [3]. The same procedure also yields the CLD in Laplace domain, allowing its numerical inversion.

Reaction name	**Chemical equation**
End group condensation	$P_x + P_y \underset{k_h}{\overset{k}{\rightleftarrows}} P_{x+y} + W$
Reversible ring formation from monomer	$P_1 \underset{k_h{}^1}{\overset{k_{c_1}}{\rightleftarrows}} C_1 + W$
Intermolecular exchange reaction	$P_x + P_{y+z} \underset{k_e}{\overset{k_e}{\rightleftarrows}} P_{x+y} + P_z$
Reversible ring formation from polymer	$P_{x+1} \underset{k_p}{\overset{k_{ce}}{\rightleftarrows}} P_x + C_1$

Table 1: Kinetic scheme of a single monomer reversible polycondensation with ring formation

CLD in linear reversible polycondensations starting from monomers will often remain close to the geometrical (Schulz-Flory) CLD, and so the influence of the approximations brought about by closure assumptions is known to be usually slight [3].

With non-linear polymerizations, approximation by a Laguerre series may converge very slowly, or even not at all, close to gel point. It may therefore be much more important to use more exact (although mathematically more complex) procedures.

Case Study I: Free Radical Polymerization with Transfer to Polymer in a CSTR

A simple description of this system is obtained by considering the following chemical groups: free radicals (A_1), sites of transfer to polymer (A_2), monomer (A_3), primary radicals (A_4), initiator (A_5) and polymerized monomer units (A_6). A more detailed analysis considering (among others) terminal branching can be found elsewhere [4], as well as the required population balance equations in Laplace domain. This kinetic scheme is summarized in Table 2. Some kinetic parameters used in the simulations are usual values for the polymerization of vinyl acetate initiated by AIBN: $f = 0.5$, $k_d = 9 \times 10^{-6}$ s^{-1}, $k_p = 1.17 \times 10^4$ dm^{3}mol^{-1}s^{-1}, $C_i = k_i/k_p = 1$ and $C_P = k_{fp}/k_p = 1.2 \times 10^{-4}$. Nevertheless, termination is supposed to occur by disproportionation and combination with equal probability: $k_t = k_{td} + k_{tc} = 2.5 \times 10^8$ dm^{3}mol^{-1}s^{-1} with $C_{tc} = k_{tc}/k_t = 0.5$.

This very simplified scheme had been chosen to illustrate the predictive capabilities of "Numerical Fractionation" (NF) [5] [6] in the original paper, but only now can the calculations by that approach be duly assessed, since no accurate solution was available at that time for non-linear free radical polymerization.

In Figures 1 and 2 are compared the predictions obtained with the present method and NF for the transient operation of a CSTR with space-time values $\tau = 50$ and 120 min (dimensionless time = t/τ). It was considered that the initial and feed concentrations of initiator and monomer were 10^{-3} and 3.57 mol dm^{-3}, respectively. The simulations

Reaction name	**Chemical equation**
Initiator decomposition	$A_5 \xrightarrow{k_d} 2fA_4$
Monomer initiation	$A_3 + A_4 \xrightarrow{k_i} A_1 + A_6$
Monomer propagation	$A_1 + A_3 \xrightarrow{k_p} A_1 + A_2 + A_6$
Transfer to polymer	$A_1 + A_2 \xrightarrow{k_{fp}} A_1$
Termination by disproportionation	$A_1 + A_1 \xrightarrow{k_{td}} products$
Termination by combination	$A_1 + A_1 \xrightarrow{k_{tc}} products$

Table 2: Kinetic scheme in a free radical polymerization with transfer to polymer

with NF were obtained by integration of the correspondent set of differential equations [5] using RADAU5 integrator with relative and absolute tolerances at the lower limit of ATOL=10^{-16} and RTOL=10^{-10}. The influence of the number of generations (NG) considered in the calculations was analyzed by varying this parameter in the simulations. It was stated before that: "no difference is discernable whether 8 or 10 generations are used and that the use of 5 generations is generally sufficient" [5]. This statement can be confirmed in Figures 1 and 2. In both cases, an upper limit of 30 generations was considered. In this case the integration fails to go throughout the gel point, but it is clear the agreement with a lower number of generations. The fact that NF converges by increasing the number of generations does not mean it approximates the true numerical solution to any prescribed accuracy: it lacks mathematical consistency.

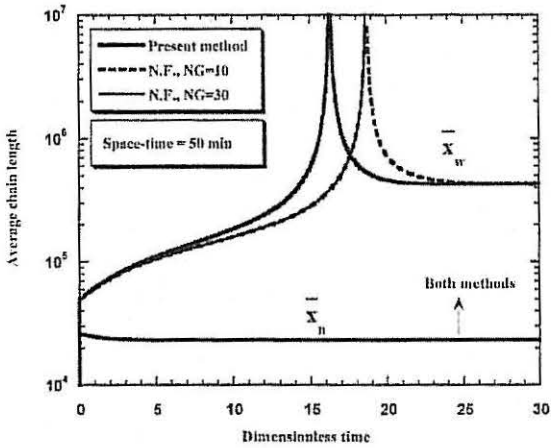

Figure 1: Comparison with exact results of predicted average chain lengths in a free-radical polymerization with transfer to polymer in a CSTR with τ = 50 min at non-steady state as computed by "numerical fractionation".

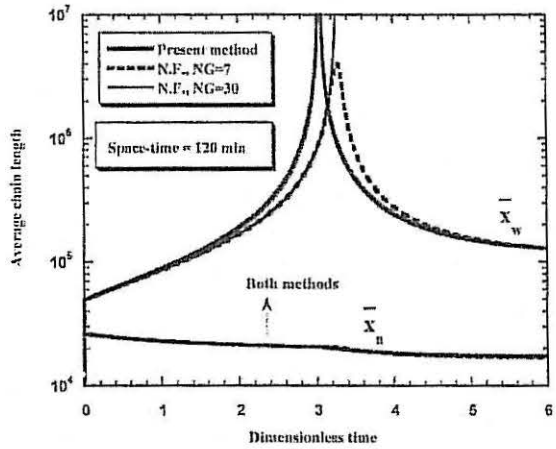

Figure 2: Comparison with exact results of predicted average chain lengths in a free-radical polymerization with transfer to polymer in a CSTR with τ = 120 min at non-steady state as computed by "numerical fractionation".

Significant differences in the predictions of the two methods occur, namely in the vicinity of the gel point. This fact is explained, in our opinion, through the improved mathematical exactness of the present method. It is free from a set of approximation conditions usually applied in the analysis of non-linear free radical polymerizations, such as the pseudo steady state for radical concentrations, the neglect of the existence of multiple radical centers and the use of closure conditions for the moments.

Case Study II: Metallocene Catalyzed Copolymerization of an Olefin with a Non-conjugated Diene

Several recent works can be found in the literature on the simulation of metallocene catalyzed olefin polymerization, where long chain branching is introduced throughout the polymerization of terminal double bonds generated by β-hydride elimination. The copolymerization of an olefin with a non-conjugated diene is suggested as a way to obtain long chain branching polyolefins under mild conditions. In this kind of systems, the polymer will contain pendant double bonds as result of the diene introduction and terminal double bonds from β-hydride elimination. An important difference between the olefin and olefin/diene polymerization systems is the ability of the latter for gelation. This case study was previously analyzed in the pre gel region by using a finite element procedure over the set of differential equations resulting from reducing the tridimensional problem to one-dimensional [7].

In this work, it is shown that the present method can be used to extend the analysis to the prediction of average chain lengths in the post gel region with gains in accuracy due to the elimination of a set of approximation conditions. A possible description of this system comprises the consideration of the following chemical groups: olefin–terminated active chain (A_1), diene–terminated active chain (A_2), pendant/ terminal double bond (A_3), olefin monomer (A_4), diene monomer (A_5), initiator (A_6), chain transfer agent (A_7), polymerized olefin unit (A_8) and polymerized diene unit (A_9). This kinetic scheme is presented in Table 3.

Reaction name	Chemical equation
Olefin initiation	$A_4 + A_6 \xrightarrow{k_{i1}} A_1 + A_8$
Diene initiation	$A_5 + A_6 \xrightarrow{k_{i2}} A_2 + A_3 + A_9$
Pendant double bond (PDB) initiation	$A_3 + A_6 \xrightarrow{k_{i3}} A_2$
Propagation PDB/olefin–terminated active chain	$A_1 + A_3 \xrightarrow{k_{p13}} A_2$
Propagation PDB/diene–terminated active chain	$A_2 + A_3 \xrightarrow{k_{p23}} A_2$
Propagation olefin/olefin–terminated active chain	$A_1 + A_4 \xrightarrow{k_{p11}} A_1 + A_8$
Propagation olefin/diene–terminated active chain	$A_2 + A_4 \xrightarrow{k_{p21}} A_1 + A_8$
Propagation diene/olefin–terminated active chain	$A_1 + A_5 \xrightarrow{k_{p12}} A_2 + A_3 + A_9$
Propagation diene/diene–terminated active chain	$A_2 + A_5 \xrightarrow{k_{p22}} A_2 + A_3 + A_9$
Chain transfer of olefin–terminated active chain	$A_1 + A_7 \xrightarrow{k_{tr1}} A_6$
Chain transfer of diene–terminated active chain	$A_2 + A_7 \xrightarrow{k_{tr2}} A_6$
β-hydride elimination from olefin–terminated active chain	$A_1 \xrightarrow{k_{\beta 1}} A_3 + A_6$
β-hydride elimination from diene–terminated active chain	$A_2 \xrightarrow{k_{\beta 2}} A_3 + A_6$
Deactivation of olefin–terminated active chain	$A_1 \xrightarrow{k_{d1}} products$
Deactivation of diene –terminated active chain	$A_2 \xrightarrow{k_{d2}} products$

Table 3: Kinetic scheme of metallocene catalyzed copolymerization of an olefin with a non-conjugated diene

Kinetic parameters used in the simulations are closely related to those considered in a previous study of this kind of systems [7], namely: $k_{p11} = k_{i1} = 10^3$ dm^{3}mol^{-1}s^{-1}, $r_1 = k_{p11}/k_{p12} = 7$, $r_2 = k_{p22}/k_{p21} = 0.1$, $C_{p1} = k_{p13}/k_{p12} = C_{p2} = k_{p23}/k_{p22} = 0.25$, $k_{p22} = 4$ dm^{3}mol^{-1}s^{-1}, $k_{i2} = k_{p12}$, $k_{i3} = k_{p13}$, $k_{\beta 1} = k_{\beta 2} = 10^{-2}$ s^{-1}, $k_{d1} = k_{d2} = 10^{-3}$ s^{-1}, $k_{tr1} = k_{tr2} = 10$ dm^{-3}mol^{-1}s^{-1}. Initial

and feed concentrations of olefin, initiator and chain transfer agent used in simulations were 1, 10^{-6} and 10^{-4} mol dm^{-3}, respectively. Mole fraction of diene was fixed in 0.2% with respect to the total monomer content.

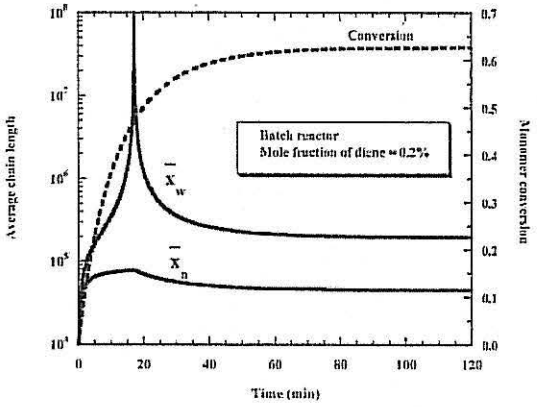

Figure 3: Average chain lengths before and after gelation for metallocene catalyzed copolymerization of an olefin with a non-conjugated diene in a batch reactor.

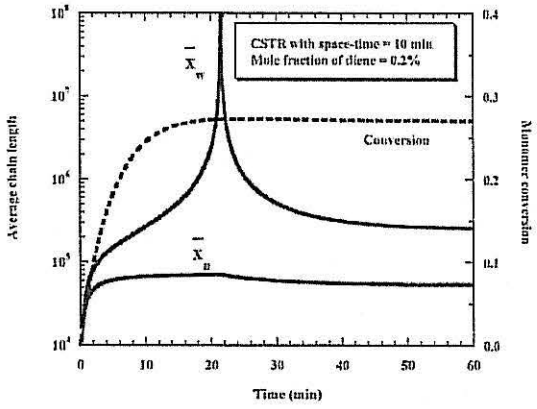

Figure 4: Average chain lengths before and after gelation for the metallocene catalyzed copolymerization of an olefin with a non-conjugated diene in a CSTR with τ= 10 min.

In Figure 3 are represented the predictions for the average chain lengths before and after gelation in batch operation. Results for the simulation of the transient behavior of a CSTR with τ=10 min are presented in Figure 4.

Conclusions

An improved method of moments, free of closure assumptions, has been shown to yield mathematically exact predictions of average molecular weights for non-linear homogeneous free-radical polymerizations, even in the presence of gel. Similar computations are also reported in this work for metallocene polymerizations.

A comparison with results obtained through "numerical fractionation" technique [5] [6] often used in recent works, has detected this latter method has problems in accurately describing polymerizations close to gel point.

A by-product of direct computation of moments is the evaluation of moment generating functions everywhere in complex space. Numerical inversion using Laplace transform methods for computing CLD becomes possible, but the choice of the best method should still be considered an open question.

Literature References

[1] M. R. P. F. N. Costa, R. C. S. Dias, *Macromol. Theory Simul.* **2003**, 12, 560
[2] H. M. Hulburt, S. Katz, *Chem. Eng. Sci.* **1964**, 19, 555
[3] M. R. N. Costa, J. Villermaux, *Ind. Eng. Chem. Res.* **1989**, 28, 702
[4] R. C. S. Dias, M. R. P. F. N. Costa, *Macromolecules* **2003**, 36, 8853
[5] F. Teymour, J. D. Campbell, *Macromolecules* **1994**, 27, 2460
[6] G. Papavasiliou, F. Teymour, *Macromol. Theory Simul.* **2002**, *11*, 533
[7] M. Nele, J. B. P. Soares, J. C. Pinto, *Macromol. Theory Simul.* **2003**, 12, 582